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Methodology for measuring trace metal surface contamination on PV silicon substrates

J. Rip[a]*, K. Wostyn[a], P. Mertens[a], S. De Gendt[ab], M. Claes[a]

[a] *Imec, Kapeldreef 75, B-3001 Leuven, Belgium*
[b] *KULeuven, Celestijnenlaan 200F,B-3001 Leuven, Belgium*

Abstract

The production of high efficiency PV cells requires a strict control on metal contamination levels. Metals like Cu and Fe are well known to cause lifetime degradation in silicon. Analytical methodologies for determination of surface metal contamination have been well established for mirror polished, also referred to as chemical mechanical polished (CMP) silicon substrates [1]. It will be explained why these methods cannot be merely applied to photovoltaic (PV) wafers because of the large roughness and specific topography of the surface. Here we extend and adapt these analytical methodologies for surface metal contamination analysis on PV substrates also referred to as PV wafers. We demonstrate how vapour phase decomposition droplet collection (VPD-DC) in combination with total reflection X-ray fluorescence spectroscopy (TXRF) or inductively coupled plasma mass spectrometry (ICP-MS) has been modified to accommodate analysis on a non-polished PV silicon wafer surface. In addition we demonstrate how metal contamination on as-cut PV wafers has been determined by liquid surface etching (LSE), i.e. an oxidizing and slow etching solution used to dissolve metal contaminants, followed by TXRF analysis. Measurements of as-cut wafers shows the presence of Fe, Cu and Zn in very high concentrations (up to more than $1x10^{13}$at/cm2), residuals of the brass-coated steel wires used during wire sawing [10].

Keywords:metal contamination; PV silicon substrate, polished, textured, as-cut, TXRF; VPD-DC, liquid surface etching

1. Introduction

In this work we present analytical methodologies for surface metal contamination analysis on PV silicon substrates. Additionally the difference in surface contamination on different surface conditions is

* Corresponding author. Tel: +32-16-28 8680; fax: +32-16-28 1706
E-mail address: Jens.Rip@imec.be

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investigated using the described methodologies. The impact of metal contamination is important for the production of high efficiency PV cells and hence requires a strict control on metal contamination levels. The need for analytical skills to investigate and monitor the metal contamination becomes important in order to help further improvement of cell efficiencies. Analytical techniques, like total reflection X-ray fluorescence spectrometry (TXRF) and inductively coupled plasma mass spectrometry (ICP-MS) in combination with wet-chemical pre-concentration procedures, are well known and widely applied for metallic contamination monitoring in semiconductor industry [1]. Vapour phase decomposition droplet collection (VPD-DC) is such a wet-chemical pre-concentration method used to improve the detection limit for metal contamination measurements using either TXRF or ICP-MS. During the VPD step, vapour HF is used to etch the native oxide on the silicon surface in order to obtain a hydrophobic surface termination [2]. In the subsequent droplet collection step, a micro droplet of a chemical mixture is moved across the wafer surface. The chemical mixture has mild oxidizing and etching properties to enable the collection of the metals from the surface without losing part of the droplet. This droplet is either analyzed directly using ICP-MS or dried on a mirror-polished surface and measured by TXRF. Some typical PV surfaces e.g. as-cut or textured are rather rough [3]. Moreover, the surface roughness makes it more difficult for smooth droplet movement and hence possibly reduces the efficiency of the collection method. Thus modification of the analytical methodology and optimization of the VPD-DC process is investigated. Since a VPD-DC process is restricted to evaluate metal contamination on top of the surface it will not give information on subsurface metal contamination. To identify subsurface metal contamination an additional liquid surface etching method (LSE) is developed to enable collection of metal contamination from surface cracks, not easily accessed by a “fast” scanning droplet as applied within the VPD-DC method.

2. Experimental

The following steps were performed to demonstrate the applicability of the VPD-DC methodology on wafers with surface terminations as-cut, alkaline textured and polished:

- Addition of controlled contamination to (PV) wafers to benchmark the performance of the analysis methodology.
- Optimization of the vapour-phase-decomposition droplet collection as pre-concentration method.
- Evaluation of TXRF and ICP-MS in combination with the surface pre-concentration method.

For the determination of subsurface metal contamination some etching liquid mixtures were evaluated for their surface etching and metal collection capacity. The LSE method is used to measure metal contamination present on mono-crystalline as-cut substrates from two different suppliers.

2.1. Controlled contamination

Semi square 125mm Cz silicon substrates with different surface topographies were intentionally contaminated with metallic traces. These traces were deposited from a liquid film of an acidified solution containing different kind of metal ions [4]. Mixtures of metal solutions were prepared by dilution of certified ICP calibration standard solutions (1000 mg/L, Merck CertiPUR®) and were acidified with nitric acid (69%, SCP SCIENCE PlasmaPURE*Plus*). The metals of interest were added in a concentration range between $1.7x10^{-7}$ and $1.7x10^{-5}$ mol/L. The hydrophilic substrates were positioned horizontally on a wafer holder and covered with 15mL aliquots of the acidified metal stock solutions. The liquid “film” was removed after 30 seconds contact time by tilting the wafer 45° and the wafer surface was dried by a flow of nitrogen through an air-knife. The final stage of drying occurs primarily through evaporation; leaving the non-volatile metallic compound on the surface. The metal deposition from an acidified solution is mainly controlled by the thickness of the evaporated layer [4]. By varying the metal concentration in the acidified liquid film the surface metal concentration can be controllably varied between 10^{10}at/cm2 to

10^{12}at/cm^2 equivalent concentration on mirror like Si surface. The concentration deposited on mirror polished silicon is determined by direct TXRF analysis with an ATOMIKA 8300W system equipped with a tungsten tube which was operated at 50 kV and 55 mA. All measurements were executed with primary X-rays incident at an angle of 2.3 mrad on the silicon surface and the analyte X-ray fluorescence was recorded during an acquisition time of 1000 seconds. The intentional contaminated wafers were further used for evaluation of the VPD-DC method.

2.2. Vapour phase decomposition droplet collection

First the applicability of HF vapour, to etch native oxide from an as-cut and textured surface compared to a polished surface, was investigated by comparing static contact angles (CA) before and after exposure to HF vapour. Droplets (10µL) of semicondutor grade ultra pure water are deposited on the surface and the static CA was determined with a Dataphysics OCAH230L system. Vapour HF was applied for 4 minutes at 10°C in the processing module of a GeMeTec (currently Munich Metrology GmbH) wafer surface preparation system (WSPS) [5][6]. Secondly, droplet collection parameters were optimized. The velocity of the scanning droplet was varied between 5 and 20 mm/s, the droplet volume was varied between 50 and 100µL and the ratio of constituent chemicals (KMG Gigabit® grade chemicals) of collection mixture, HF (0.5 wt.%)/H2O2 (1 wt.%)/H2O (98.5 wt.%). [1], was adjusted to enable smoother movement of the collection droplet over the surface of as-cut and textured PV wafers. The droplet scanning area was circular shaped with an edge exclusion of 2 mm and the droplet scanning pattern was a spiral starting from the wafer centre. The scanned area of the 125mm wafer covered ~75% of the total wafer area. The collection droplet can be split [5] and one part dried at 50°C 100hPa on mirror polished silicon for TXRF analysis (TXRF analysis parameters are described above). The remaining liquid can be transferred into dedicated vials for subsequent ICP-MS analysis (results not shown here).

2.3. Liquid surface etching method

The wafer surface was uniformly covered with a known volume of a chemical solution and the chemical puddle; figure 1, was recuperated after 10 minutes contact time. Aliquots of the puddle solution were transferred on mirror polished silicon wafers and further analysed by direct TXRF (TXRF analysis parameters are described above). The etch rates for a dilution series of a chemical mixture HF/HNO3/HCl 3/9/27 was evaluated. [7] A 5 times diluted mixture (KMG Gigabit® grade chemicals) with respective etch rate ≤ 1nm/min was retained for evaluation of metal liquid surface etching (LSE) on as-cut wafers.

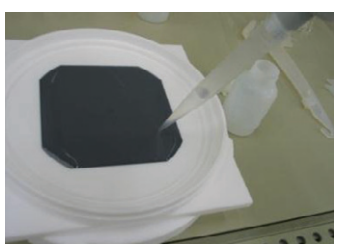

Fig. 1. Recuperation of chemical puddle on top of as-cut wafer topography after liquid surface etching.

3. Results

3.1. VPD-DC

The applicability of vapour HF to etch native oxide from the surface of as-cut and textured wafers was investigated by determining the static contact angle of water. Table 1 shows increased contact angles after exposure to vapour HF during 4 minutes. Contact angles of as-cut and textured surface finish were even higher compared to polished silicon. Such enhanced values could be due to the surface topography [8] [9]

Table 1. Static contact angle (°) of water for different silicon surface topographies before and after contact with HF.vapour.

Surface topography	before HF vapour	after HF vapour
Polished	<15	62.0
As-cut	17.0	90.9
Textured	36.5	75.9

With a scanning velocity set to 5mm/s we were able to move droplets with volumes of 50µL up to 100µL ± 1µL, of collection mixture with ratio 10/3/96 of respectively HF (49 w%), H_2O_2 (30 w%) and H_2O, over the surface of as-cut and textured PV wafers. The volumetric droplet loss, as percentage of the starting volume was determined from a post scanning volume measurement by the WSPS equipment. Table 2 reports the volumetric loss (average of 5 replicates) for as-cut and textured topography in report to a polished wafer surface. There is a significant difference in droplet volume loss when increasing the surface topography. This increase in volume loss is included in a correction factor when analyzing the surface contamination.

Table 2. Volumetric droplet loss as % of the starting volume for different surface topographies

Surface topography	% volume loss
Polished	2.7 ± 1.5
As-cut	19.0 ± 0.9
Textured	10.3 ± 0.7

3.2. VPD-DC-TXRF

The analysis methods have been developed and evaluated for polished, as-cut and alkaline textured wafers using the controlled addition of metal contamination. VPD-DC-TXRF efficiencies have been established for several elements as the ratio of the concentration determined by the VPD-DC-TXRF method to the deposited concentration determined by direct TXRF analysis on the polished surface. For some metals, e.g. nickel (Ni), the surface metal concentration recovered on controlled contaminated wafers is slightly higher than the metal concentration measured on polished wafers. The main difference is the detection of a non-negligible background contamination. When correcting for the background contamination, the VPD-DC-TXRF efficiency, e.g. ~80% for Ni, is comparable for as-cut, alkaline textured and polished wafers. VPD-DC-TXRF efficiencies for some other metals, e.g. iron (Fe), could not be determined by the controlled contamination. The surface concentration of Fe is much higher and nearly constant for the as-cut or alkaline textured wafers compared to the polished wafers as shown in Figure 2. This is an indication of large initial surface concentrations of e.g. Fe which precludes a precise determination of the VPDDC-TXRF efficiency. The efficiency on textured wafers was estimated from subsequent VPD-DC-TXRF analysis. The concentration remaining after the first VPD-DC-TXRF process was determined by a subsequent VPD-DC-TXRF analysis. Table 3 lists the remaining concentration as percentage of the total concentration of two subsequent VPD-DC-TXRF measurements. The VPD-DC-

TXRF efficiency on as-cut topography was estimated by combining VPD-DC-TXRF followed by liquid surface etching to determine remaining metals on as-cut wafers (see paragraph 3.3).

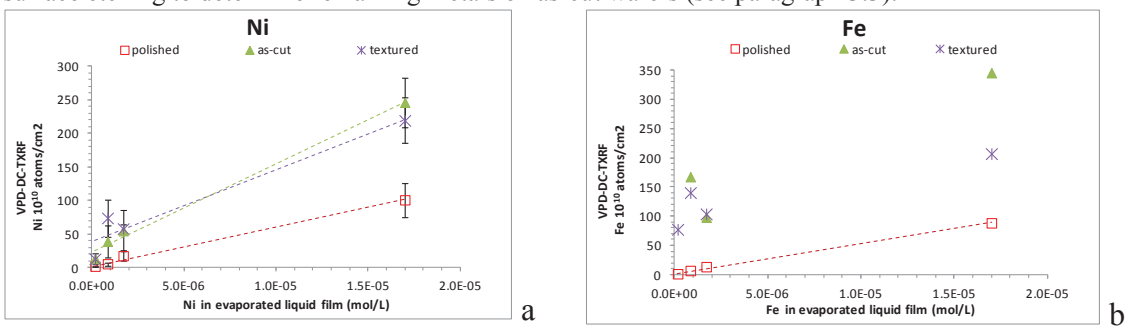

Fig. 2. Surface metal concentration as function of added contamination for Ni (a) and for Fe (b)

Table 3. Estimation for VPD-DC-TXRF efficiency: % remaining on textured surface after subsequent VPD-DC-TXRF analysis. Average of 3 samples, one of each concentration: 5.10^{10}-1.10^{11}-1.10^{12} atoms/cm^2

Remained after oneVPD-DC-TXRF sequence	K	V	Fe	Co	Ni	Cu	Zn
Average of 3	1.6 ± 1.6	2.2 ± 1.5	13.9 ± 11.9	3.0 ± 0.7	8.0 ± 5.9	36.9 ±21.1	3.3 ± 0.6

3.3. Liquid surface etching of as-cut wafers

Figure 3 shows the percentage of metals recovered from as-cut wafers using VPD-DC-TXRF followed by three sequential liquid surface etching (LSE) steps. Approximately 60% of the Fe concentration could be recovered by the VPD-DC-TXRF method, which is significantly lower than the VPD-DC-TXRF efficiency of ~90%.obtained on polished wafers. This significantly lower efficiency for Fe on as-cut wafers indicates either that iron is present in a chemical state which is different from the Fe added during controlled contamination experiments or that the is present in a location on the as-cut wafer that cannot be reached by the VPD-DC, e.g. inside micro-cracks of the as-cut wafer. 80% of the remaining Fe could be collected in the first LSE step, indicating the applicability of the liquid surface etching method for the detection of surface metal concentrations on as-cut wafers. The surface metal concentrations have been measured on as-cut wafers from 2 different vendors. The results in Table 4 show surface metal concentrations up to more than 1x10^{12}at/cm2 for iron, copper and zinc. This is reminiscent of the wire sawing where a brass-coated (Cu/Zn alloy) steel wire is used together with an abrasive, either suspended (e.g. SiC) or deposited on the wire (e.g. diamond) [10].

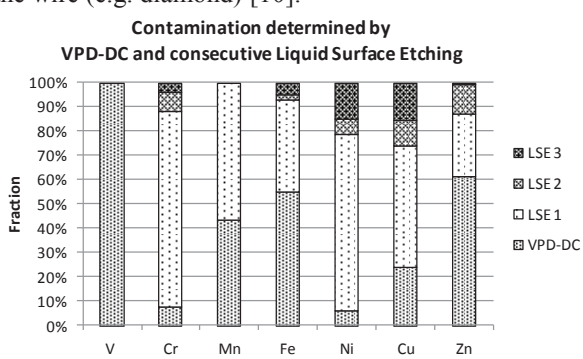

Fig. 3. Fractions of contamination determined by VPD-DC and by Liquid Surface Etching of as-cut wafers

Table 4. As-cut surface contamination determined by TXRF analysis of the liquid surface etching solution

Surface concentration (10^{10} atoms/cm^2)	Cr	Fe	Ni	Cu	Zn
Supplier A	10-12	14-1700	11-16	200-1700	45-120
Supplier B	8-15	3300-4600	33-37	1300-1900	280-390

4. Conclusions

The analytical methodology, VPD-DC combined with TXRF or ICP-MS, which is used in semiconductor industry for determination of surface metal contamination on mirror polished silicon substrates has been successfully extended towards PV silicon wafers. Metal contamination was deposited under controlled conditions and effectively recovered from textured PV topography by droplet collection (VPD-DC). Consecutive liquid surface etching steps applied after VPD-DC on as-cut topography showed significant lower droplet collection efficiency for e.g. iron in report to polished and textured wafers. This could be due to the chemical state of metals, residuals of wire sawing, being different from the metal contamination as applied during controlled contamination experiments or to the location of the metal species on as-cut topography. Metal contamination, located in e.g. micro-cracks, which cannot be reached by the VPD-DC method were efficiently determined by the liquid surface etching method on as-cut wafers from 2 different suppliers.

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